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Unit 3: Chemical bonding

3.1 electronegativity and bonding

Electronegativity: the power of an atom to attract electrons itself

Factors influencing the electronegativities of elements:

Nuclear charge
Atomic radius
inner electron shielding by inner shells and subshells

trends in electronegativity:

across a period, the electronegativity increases as the number of charges on the nucleus increases, allowing it to attract a bonding pair of electrons more strongly

down a group, the electronegativity decreases as there are more electron shells added, which increases the electron shielding. Atomic radius also increases down the group meaning the distance between the bonding pairs and the nucleus increases, making the attraction between them gets weaker

the electronegativities of two atoms bonded together can determine the type of bonding occurring:

if they are of equal electronegativities or a difference of less than 0.5, they have the same tendency to attract the bonding pair of electrons, so they share the electrons evenly between them and form a "pure" covalent bond. Examples include H_2 or Cl_2

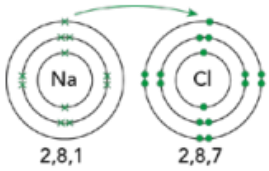
if one of the atoms is slightly more electronegative that the other or the electronegativity is between 0.5 and 1.6, is attracts more than its fair share of electron density so it becomes slightly negative, and the other atom becomes slightly positive. This is described as a "polar" bond. Example: HCl

if one of the atoms is a lot more electronegative than the other or the electronegativities is greater than 2.0, the electron pair is dragged to it's end of the bond and the more electronegative atom has complete control over both electrons and ions are formed, making this an Ionic bond. There is clear difference on when a bond stops being covalent and becomes ionic, as some ionic compounds have covalent characteristics Examples: NaCl and MgF

if the electronegativity difference is between 1.6 to 2.0, if there is a metal involved, its considered ionic and if there's a non-metal involved its considered polar covalent

3.2 ionic bonding

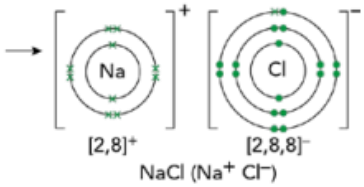
Ionic bonding: the electrostatic attraction between oppositely charged ions



Example: sodium chloride:

Sodium initially has an electronic configuration of: $1s^2\ 2s^2\ 2p^6\ 3s^1$ and

Chlorine initially has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$



In order for these two elements to be fully stable, sodium has to lose one electron to have a filled second shell, and chlorine has to gain one electron, so the final configuration of them is $1s^2\ 2s^2\ 2p^6$ and $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, respectively

They are being held together by electrostatic attractions between the positive cations and negative anions

The charge on an ion is determined by the group number and in order to have a full noble gas electronic configuration (except for Fe^{3+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Pb^{2+})

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3.3 metallic bonding

Metallic bonding: the electrostatic attraction between positive metal ions and delocalized electrons, which are delocalized over the whole metal structure, meaning they are no longer attached to an atom

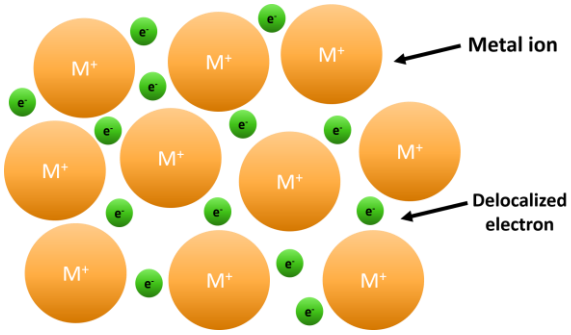
Trends in metallic strength:

Across a period, it increases as the number of electrons in the outermost shells increases so there are more delocalized electrons per atom. Group 1 metals are also inefficiently packed (8-coordinated) so they aren't forming as many bonds

Down a group, it decreases as atomic radius (distance of outer electrons and nucleus) and nuclear strength increases so the strength of the electrostatic attraction between the delocalized electrons and the nucleus is weaker. There are also more electron shells added, which causes higher electron shielding which repels the electrons away and weakens the metallic bond

Characteristics:

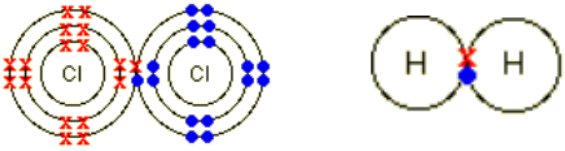
Good thermal and electrical conductors
Highly malleable (can be bent into shape/sheets)
Ductile (can be made into wires)
Have high melting and boiling points
React with acids to produce salts and hydrogen
React with oxygen to produce metal oxide and hydrogen
React with cold water/steam to produce a metal hydroxide
Metal oxides and hydroxides are basic



Alloys:
brass --> copper + zinc
stainless steel --> iron, and other elements such as chromium, nickel and carbon.

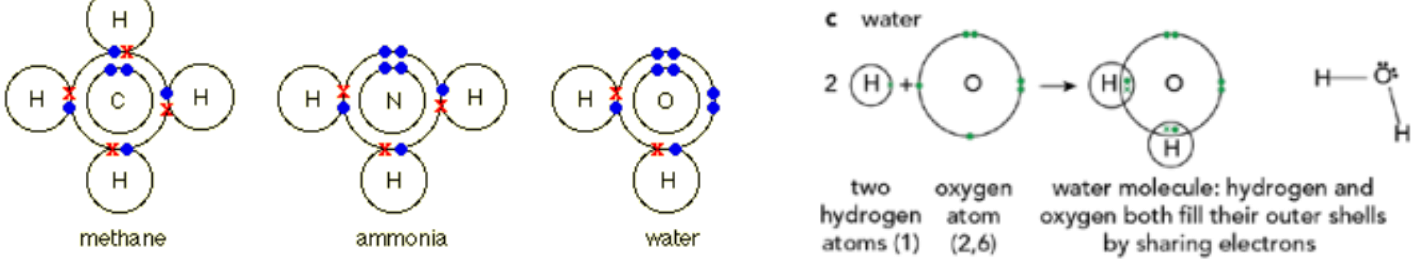
3.4 covalent bonding and coordinate bonding

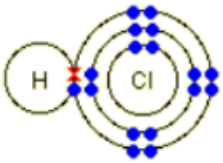
Covalent bonding: electrostatic attraction between the nuclei of two atoms and a shared pair of electrons

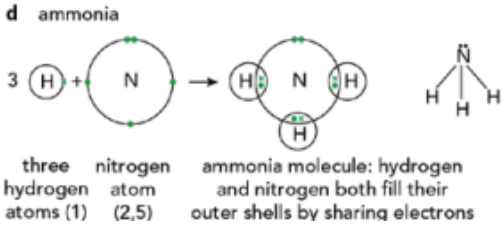


Examples and explanations:
O_2 H_2 N_2 and Cl_2 all share the same structure
Each atom shares one electron and they are shared equally between them and their outermost electron shell is filled so that each atom has a noble gas configuration

HCl, CH_4 NH_3 H_2O are bonded in a way that all the atoms also have a noble gas electronic structure







The greater the **electron density** between atoms, the stronger the attractive force, which means that atoms are pulled in further towards each other leading to a shorter bond

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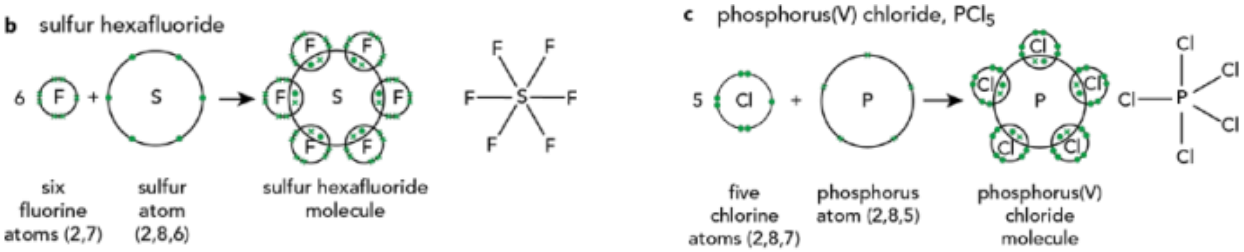
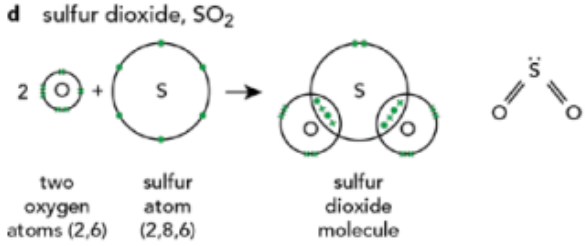
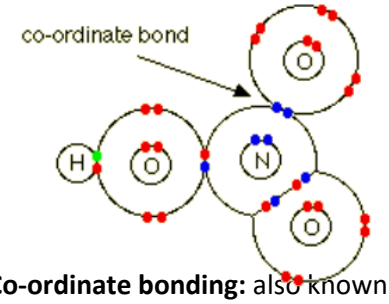
3.4 covalent bonding and coordinate bonding

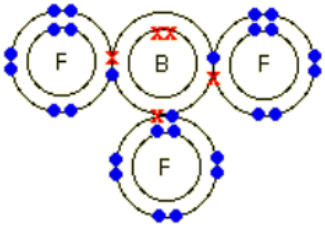
Elements in period three can expand their octet, such as in SO_2, PCl_5, SF_6, this means that their outermost shell can hold more than 8 electrons, this is due to the empty 3d subshell that is present so they do not conform to the noble gas notation





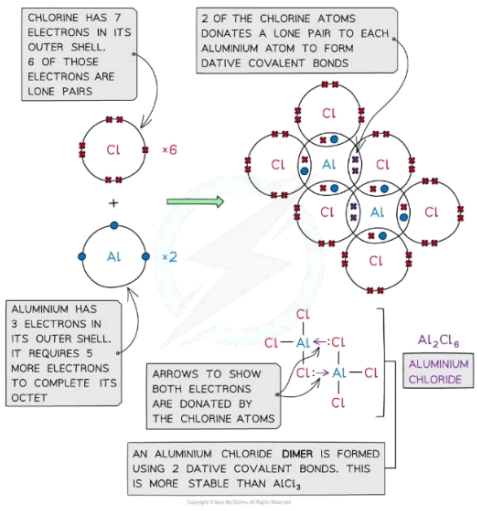
Another exemption from the noble gas notation is Boron trifluoride BF_3 and aluminum chloride at high temperatures Al_2Cl_3
In this case, boron only has 6 electrons in its outermost shell rather than 8. Energy is released when a covalent bond is formed, so when the bond is made it becomes more stable



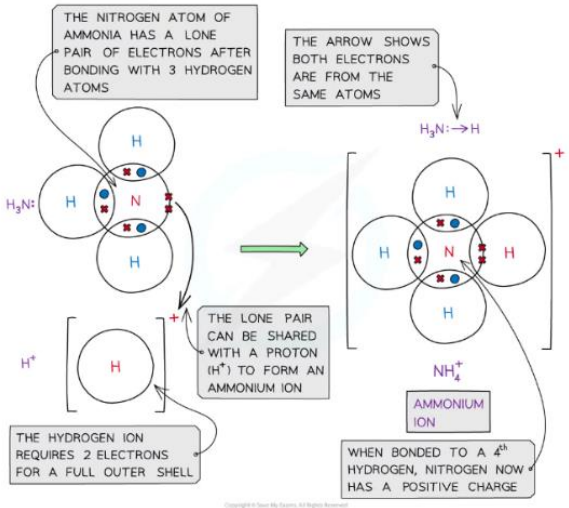


Co-ordinate bonding: also known as dative bonding is formed by two atoms sharing a pair of electrons, but rather than one electron coming from each atom, both electrons are from the same atom
This is as some molecules have a lone pair that can be donated to form a bond with an electron deficient atom
An electron deficient atom is an atom that has an unfilled outer orbital
Examples include NH_4^+, Al_2Cl_3 and CO

At high temperatures, aluminum chloride can exist as a monomer with a structure of AlI_3 but it is electron deficient
At low temperatures, two molecules of $AlCl_3$ join together to form a dimer and two co-ordinate bonds are formed
Another example of a co-ordinate bond is the hydroxonium ion which is formed when HCl dissolves in water



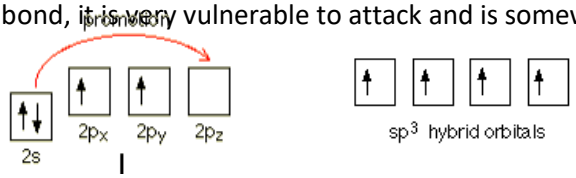
Aluminium chloride is also formed with a dative covalent bond in which two of the chlorine atoms donate their lone pairs to each of the aluminium atoms to form a dimer



Ammonia (NH_3) can donate a lone pair to an electron-deficient proton (H^+) to form a charged ammonium ion (NH_4^+)

3.4 covalent bonding and coordinate bonding

Covalent bonds occur due to the overlap of orbitals, there are two types of overlap, sigma and pi bonds
Sigma bonds are formed by direct overlap of orbitals between the bonding atoms
Pie bonds are formed by the sideways overlap of adjacent p orbital above and below sigma bonds, it is a region of space in which you can find two the two electrons that make up the bond, it is very vulnerable to attack and is somewhat distant form the control of the nuclei, and is weak than sigma bonds



In H_2 C_2H_6 C_2H_4 HCN and N_2:

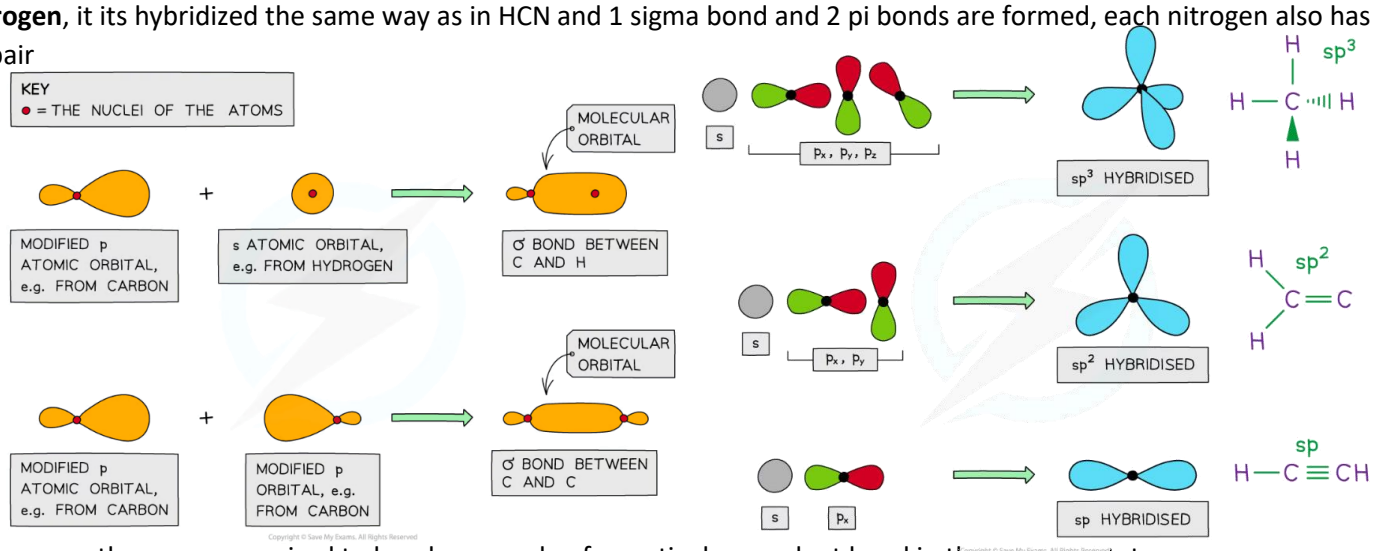
H_2 is formed when the 1s orbital of each hydrogen directly overlaps, no hybridization occurs here

Methane is formed when the central carbon, which has an electronic configuration of $1s^2$ $2s^2$ $2p^2$ gets energized/excited so one of the electrons in 2s orbital gets promoted to the empty 2p orbital and forms a "new" shell known as the sp^3, this allows each of the 1s orbitals of each hydrogen to directly overlap with each orbital in the sp^3 shell forming 4 sigma bonds
In **ethane**, both carbons also get hybridized in the same way as methane does, and three of them bond directly with the 6 hydrogens, the last orbital however bonds with its similar one on the other carbon, creating an end-to-end overlap and creating another sigma bond, this means that in total, ethane has 7 sigma bonds
All **alkanes** are bonded the same way with the carbon atoms promoting an electron and hybridizing to give sp^3 hybrid orbitals, the carbon atoms will join each other by forming sigma bonds by the end-to-end overlap of their sp^3 hybrid orbitals, hydrogen atoms will join wherever they are needed by overlapping their $1s^1$ orbitals with sp^3 hybrid orbitals on the carbon atoms

In **ethene**, the carbon atom doesn't have enough unpaired electrons to form the number of required bonds, so it promotes one of the $2s^2$ electrons into the empty 2p orbital, this causes the carbon to be in an excited state and having four unpaired electrons, however since the carbon is only joining to three other atoms, it only hybridizes three of the orbitals rather than all four, using the 2s electron and two of the 2p electrons, but the third one unchanged, this causes the formation of the sp^2 hybrid orbital as it is made of one s orbital and two p orbitals. These three hybrid orbitals arrange themselves in a way which makes them exactly 120 degrees apart in a plane, and the remaining p orbital is at right angles to them, this causes the creation of sigma bonds which are formed by end-to-end overlap of the carbon atoms and the hydrogen atoms, the p orbitals that were unhybridized also overlap sideways, creating a pi bond. Ethene is a planar molecule so there is no free rotation about the carbon-carbon double bond

In **HCN**, nitrogen has the electronic structure of $1s^2$ $2s^2$ $2p^3$. Since it will form a triple bond, it hybridizes to give sp^1 hybrid orbitals, leaving two of the p orbitals unchanged and containing a lone pair of electrons, the nitrogen now joins to a carbon with a hydrogen attached, and sigma bond is formed between the two nuclei, and 2 pi bonds form by sideways overlap of the two unhybridized p orbitals of nitrogen and 2 p orbitals in carbon. The bonds are at right angles to each other

In **nitrogen**, it its hybridized the same way as in HCN and 1 sigma bond and 2 pi bonds are formed, each nitrogen also has a lone pair



Bond energy: the energy required to break one mole of a particular covalent bond in the gaseous state
Bond length: the internuclear distance of two covalently bonded atoms

$$X\text{-}Y(g) \longrightarrow X(g) + Y(g)$$

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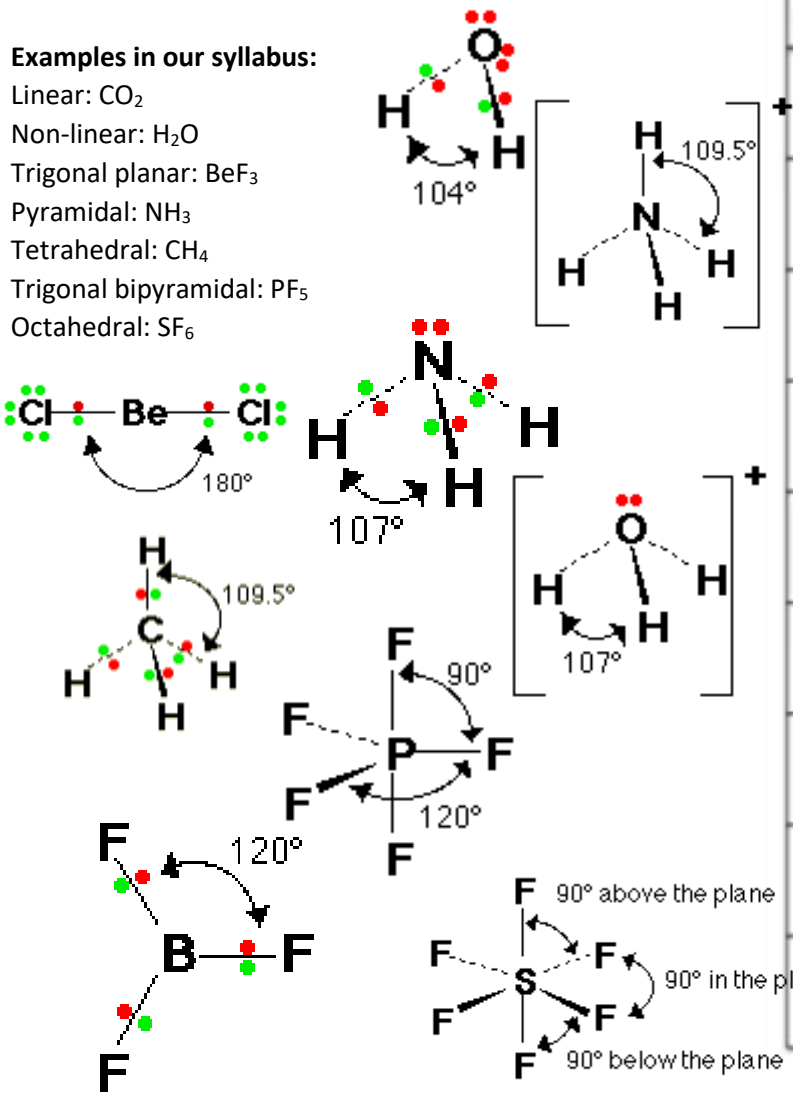
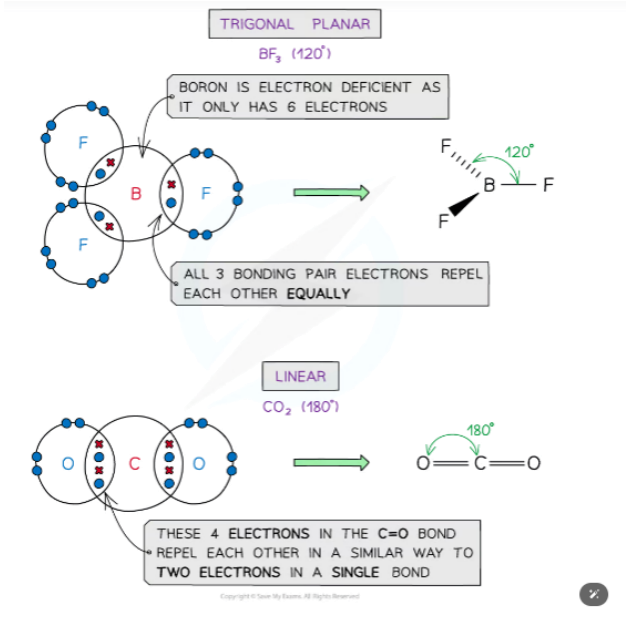
3.5 Shapes of molecules

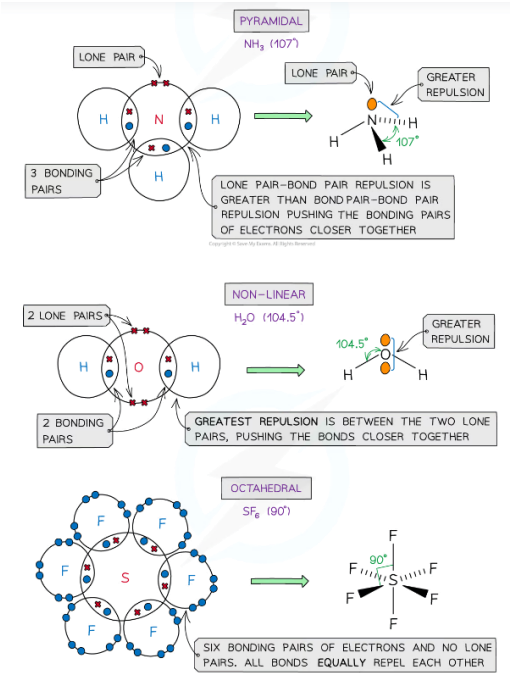
How to figure it out: from number of bonded electrons and lone pairs

Examples in our syllabus:
Linear: CO_2
Non-linear: H_2O
Trigonal planar: BeF_3
Pyramidal: NH_3
Tetrahedral: CH_4
Trigonal bipyramidal: PF_5
Octahedral: SF_6



bonding pairs	lone pairs	shape and bond angles
2	0	linear
2	1	non-linear 120 – 2.5 = 117.5°
2	2	non-linear 109.5 – 2 x 2.5 = 104.5°
3	0	trig. planar
3	1	pyramidal 109.5 – 2.5 = 107°
4	0	tetrahedral
4	2	square planar
5	0	trig. bipyramidal
6	0	octahedral





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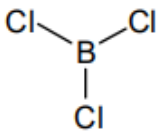
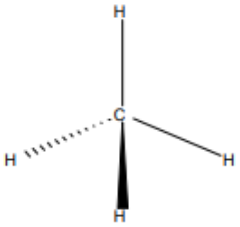
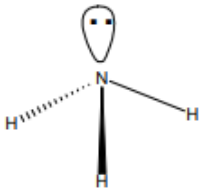
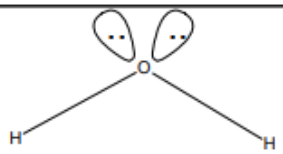
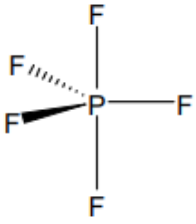
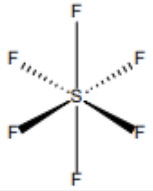
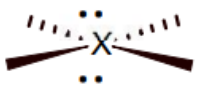
Name	No bonding pairs	No lone pairs	Diagram	Bond angle	Examples
linear	**2**	**0**	Cl—Be—Cl	**180**	CO_2, CS_2, HCN, BeF_2
Trigonal planar	**3**	**0**		**120**	BF_3, $AlCl_3$, SO_3, NO_3^-, CO_3^{2-}
Tetrahedral	**4**	**0**		**109.5**	$SiCl_4$, SO_4^{2-}, ClO_4^-, NH_4^+
Trigonal pyramidal	**3**	**1**		**107**	NCl_3 ,PF_3 ,ClO_3 ,H_3O^+
Bent	**2**	**2**		**104.5**	OCl_2, H_2S, OF_2 , SCl_2
Trigonal Bipyramidal	**5**	**0**		**120 and 90**	PCl_5
Octahedral	**6**	**0**		**90**	SF_6



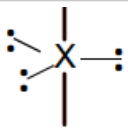
Square planar
Bond angle 90°

e.g XeF_4

Xe has 8 electrons in its outer shell. 4 F's add 4 more electrons. This makes a total of 12 electrons made up of 4 bond pairs and 2 lone pairs. The means it is a variation of the 6 bond pair shape (octahedral)

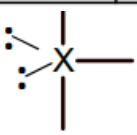
Bond angle ~89°
(Reduced by lone pair)

e.g. BrF_5



Bond angle 180°

e.g I_3^-



Bond angle ~89°
(Reduced by lone pairs)

e.g. ClF_3

Cl has 7 electrons in its outer shell. 3 F's add 3 more electrons. This makes a total of 10 electrons made up of 3 bond pairs and 2 lone pairs. The means it is a variation of the 5 bond pair shape (trigonal bipyramidal)

Bond angles ~119 + 89°
(Reduced by lone pair)

e.g. SF_4 & IF_4^+

I has 7 electrons in its outer shell. 4 F's add 4 more electrons. Remove one electron as positively charged. This makes a total of 10 electrons made up of 4 bond pairs and 1 lone pair. The means it is a variation of the 5 bond pair shape (trigonal bipyramidal)

3.6 Intermolecular forces, electronegativity and bond properties

Van der Waals' forces: the intermolecular forces between molecular entities other that those due to bond formation, they are generally intermolecular forces. They are attractions between a molecule and its neighboring molecule, and is different from the bonds that HOLD molecule together such as covalent bonds which are known as intramolecular attractions
They are what determines the state of a molecule and its melting and boiling points

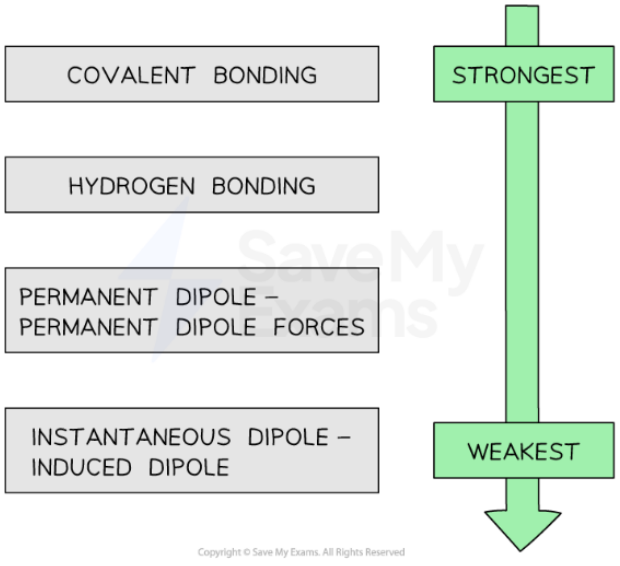
The three types of van der Waals forces are: instantaneous dipole-induced dipole (ID-ID) also known as London dispersion forces, permanent dipole-permanent dipole (PD-PD) and hydrogen bonding which falls under PD-PD

Instantaneous dipole-induced dipole forces occur due to temporary fluctuating dipoles, and in molecules which are symmetrical thus have no electrical distortion to produce negative or positive parts such as H_2 or Br_2 as they are also non-polar. Yet, as the electrons are mobile, at one instant they may find themselves at one end of the molecule making it slightly negative and the other end slightly positive, an instant later this is reversed, this happens instantaneously and is random. This effect can give rise to intermolecular attractions as when a molecule has a slightly charged end for an instant, this will cause the molecules near it to also be charged and in the opposite way, setting up an induced dipole that attracts the molecules to each other.
The size of each molecule affects the strength of the dispersion forces, an example can be used through the boiling points of the noble gases which exist as single atoms, the bp increases down the group meaning the ID-ID forces are greater, this is due to the fact that the number of electrons and the size of the atom increases, which causes a greater electron shielding and distance from the nucleus
The shape of each molecule affects the strength of the dispersion forces, they are most effective in long thin molecules rather than branched molecules.

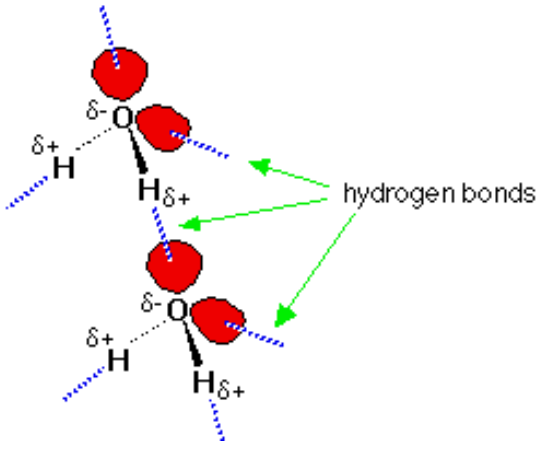
Permanent dipole-permanent dipole forces only occur in polar molecules where the electronegativity difference between the atoms bonded together is great and the molecule is not symmetrical, they occur IN ADDITION to ID-ID forces

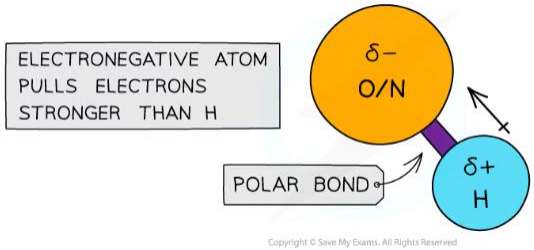
Hydrogen bonding is a special type of ID-ID forces in molecules containing N-H and O-H, this is because nitrogen and oxygen causing the hydrogen to acquire a significant amount of positive charge. The main examples of hydrogen bonding is water and ammonia. Each water molecule can have 4 hydrogen bonds which allows it to have a high melting and boiling point relative to other covalent structures, it also allows it to have high surface tension due to cohesion between the water molecules, alcohols also have hydrogen bonding.

Ionic, covalent, metallic, hydrogen bonds, PD-PD and ID-ID forces, from most to least powerful



The varying strengths of different types of bonds





Extra page for pastpapers notes

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